

X-Ray Diffraction and Melting Point-Composition Studies on the 9,10-Epoxy- and Dihydroxystearic Acids and 9,10-Epoxyoctadecanols²

BY LEE P. WITNAUER AND DANIEL SWERN

This paper reports the results of X-ray diffraction and melting point-composition studies on the isomeric 9,10-epoxy- and dihydroxystearic acids, and the isomeric 9,10-epoxyoctadecanols. The need for such an investigation arose from two independent lines of work being pursued in our laboratory. First, it was desired to use X-ray diffraction methods to obtain direct proof of the validity of certain conclusions regarding the stereochemistry of some of these long-chain compounds.³ Second, a means of analyzing mixtures

of isomeric pairs would be of value in studies of the mechanism of the reaction of oleic acid, methyl oleate, and oleyl alcohol (and their *trans* isomers) with oxygen,⁴ since mixtures of isomeric 9,10-epoxy compounds and 9,10-dihydroxy compounds are obtained which can be positively identified at present only after numerous fractional crystallizations, and isolation of the individual products. Naturally, in such a purification procedure, loss of product occurs, much time is consumed, and the product most readily isolated is the less soluble of a given isomeric pair, the other isomer usually being isolated in poor yield, if at all.

As is well known, melting point-composition diagrams have been used to determine the composition of binary mixtures. The technique is simple and convenient, and in many cases the

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(2) This paper is number XI in the series, Chemistry of Epoxy Compounds. For paper X, see *THIS JOURNAL*, **71**, 3849 (1949). This paper was presented at the 117th Meeting of the American Chemical Society, Philadelphia, Pa., April 9-13, 1950.

(3) Swern, *ibid.*, **70**, 1235 (1948).

(4) Knight and Swern, *J. Am. Oil Chem. Soc.*, **26**, 366 (1949).

accuracy is high (composition determined to ± 1 mole per cent.). We tried this technique with the three isomeric systems under investigation. As shown later, it was successful with the isomeric 9,10-epoxyoctadecanols and 9,10-epoxystearic acids, but not with the 9,10-dihydroxystearic acids. For the 9,10-dihydroxystearic acids, the composition of binary mixtures was measured by an X-ray diffraction method. We have been unable to find any references in the literature that describe X-ray diffraction or melting point-composition studies on the three isomeric systems reported here.

Experimental

Preparation of Materials.—The isomeric 9,10-epoxystearic acids, m. p. 58.1–58.7° and 54.1–55.0°, were prepared by the peracetic acid oxidation⁵ of oleic⁶ and elaidic⁷ acids, respectively. Contrary to some published reports,^{8,9} these acids do not have the same melting points. The isomeric 9,10-epoxyoctadecanols, m. p. 52.6–53.5° and 48.0–48.8°, were prepared by the peracetic acid oxidation⁵ of oleyl¹⁰ and elaidyl¹⁰ alcohols, respectively. The isomeric 9,10-dihydroxystearic acids, m. p. 130.7–131.0° and 94.7–

TABLE I

X-RAY DIFFRACTION PATTERNS OF HIGH AND LOW MELTING 9,10-DIHYDROXYSTEARIC ACIDS AND OF A MIXTURE CONTAINING 75% LOW MELTING AND 25% HIGH MELTING ISOMERS

Mixture of 75% low melting and 25% high melting isomers		9,10-Dihydroxystearic acid, m. p. 95°		9,10-Dihydroxystearic acid, m. p. 131°	
<i>I</i> obs.	<i>d</i> , Å.	<i>I</i> obs.	<i>d</i> , Å.	<i>I</i> obs.	<i>d</i> , Å.
M ⁻	20.93			S	20.89
S	19.48	S ⁺	19.54		
M	13.94			S ⁺	13.95
S ⁻	13.02	S	13.06		
M ⁺	10.42			S ⁺⁺	10.43
S	9.76	S ⁺	9.77		
W ⁺	8.35			M	8.36
W ⁻	7.82	W	7.81		
W	6.95			M	6.96
M ⁻	6.51	M	6.51		
W ⁻	5.99			W ⁻	5.96
W ⁻	5.60	W	5.60		
W	5.25			W ⁺	5.23
W	5.11	W ⁺	5.09		
W ⁻	4.99	W ⁻	4.96		
W ⁻	4.89	W ⁻	4.89		
W ⁻	4.66			W ⁻	4.64
M ⁺	4.52	S ⁻	4.52		
W ⁻	4.37	W ⁻	4.43		
W ⁻	4.29	W	4.28	W (diff.)	4.29
M ⁻	4.19			M ⁺	4.18
S ⁻	4.11	S ⁺⁺	4.11		
W (diff.)	3.94	M ⁻	3.92	W	3.97
W ⁺	3.60	M ⁻	3.62		
W ⁺	3.53			W ⁺	3.54

(5) Findley, Swern and Scanlan, *THIS JOURNAL*, **67**, 412 (1945).

(6) (a) Brown and Shinowara, *ibid.*, **59**, 6 (1937); (b) Wheeler and Riemenschneider, *Oil and Soap*, **16**, 207 (1939); (c) Swern, Knight and Findley, *ibid.*, **21**, 133 (1944).

(7) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

(8) Nicolet and Poulter, *THIS JOURNAL*, **52**, 1186 (1930).

(9) Atherton and Hilditch, *J. Chem. Soc.*, 204 (1943).

(10) Swern, Jordan and Knight, *THIS JOURNAL*, **68**, 1673 (1946).

95.1°, were prepared by the hydrogen peroxide-acetic acid-sulfuric acid oxidation of oleic and elaidic acid, respectively.¹¹

X-Ray Technique.—Powder patterns of the pure isomers and the mixtures described below were recorded with a powder camera of 14 cm. diameter; chromium $K\alpha$ radi-

TABLE II

X-RAY DIFFRACTION PATTERNS OF ISOMERIC 9,10-EPOXYSTEARIC ACIDS

<i>trans</i> -9,10-Epoxyoctadecanoic acid, m. p. 54–55°		<i>cis</i> -9,10-Epoxyoctadecanoic acid, m. p. 58.1–58.7°	
<i>I</i> obs.	<i>d</i> , Å.	<i>I</i> obs.	<i>d</i> , Å.
W	23.59	S ⁺⁺	22.65
S ⁺⁺	15.72	M	11.33
M	11.83	W	7.98
M	9.43	M	7.57
W	7.86	W	7.14
M ⁻	6.72	W ⁻	6.64
W ⁻	5.88	W ⁻	6.39
W ⁻	5.62	W	6.29
W	5.23	W ⁻	5.71
M	4.71	W	5.05
S ⁺⁺	4.30	W ⁻	4.68
M ⁻	4.18	W ⁺	4.54
M ⁺	4.06	W (diff.)	4.40
W ⁺	3.93	S	4.28
W	3.80	S	4.12
S	3.63	S ⁻	4.01
W (diff.)	3.51	M ⁻	3.91
W	3.37	M ⁻	3.83
W ⁻	3.21	M ⁺	3.71
		W	3.44
		W (diff.)	3.37
		W	3.31
		W	3.26

TABLE III

X-RAY DIFFRACTION PATTERNS OF ISOMERIC 9,10-EPOXYOCTADECANOLS

<i>trans</i> -9,10-Epoxyoctadecanol, m. p. 48.0–48.8°		<i>cis</i> -9,10-Epoxyoctadecanol, m. p. 52.6–53.5°	
<i>I</i> obs.	<i>d</i> , Å.	<i>I</i> obs.	<i>d</i> , Å.
S ⁺⁺	24.65	S ⁺⁺	22.49
M ⁺	16.47	S	14.99
W	12.36	W	11.24
W ⁺	9.88	M ⁺	9.00
M	8.23	M ⁺	7.50
W ⁺	7.08	W ⁺	6.43
W ⁻	6.41	W ⁻	5.63
W	5.71	W ⁺	5.00
W	5.50	W ⁺	4.51
W ⁻	5.30	W	4.23
M ⁻	4.95	M	4.09
W ⁺	4.53	M ⁻	3.87
W ⁻	4.24	W ⁺	3.63
S ⁺	4.13	W (diff.)	3.48
W ⁻	4.05	W (diff.)	3.34
W ⁻	3.99	W ⁻	3.22
W (diff.)	3.87	W ⁻	3.09
S ⁻	3.69	W ⁻	2.82
W ⁻	3.55	W ⁻	2.78
W ⁻	3.49		
W ⁻	3.41		

(11) Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

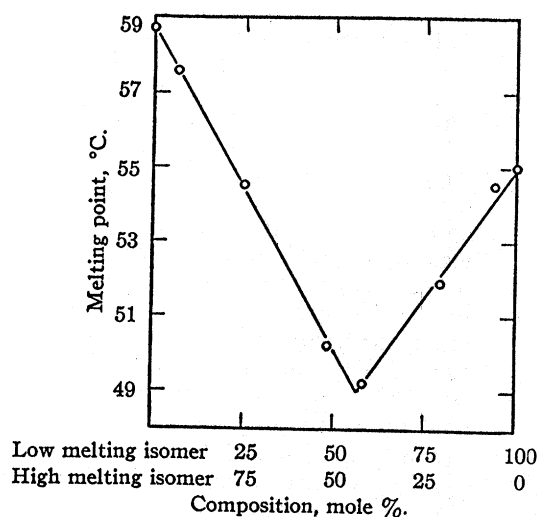


Fig. 1.—9,10-Epoxysearic acids, melting point-composition.

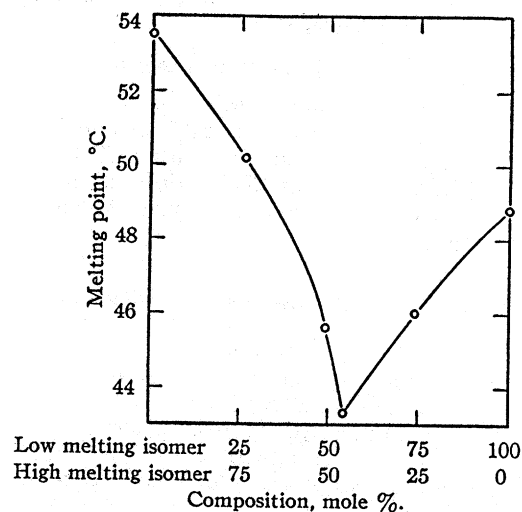


Fig. 2.—9,10-Epoxyoctadecanols, melting point-composition.

tion was used. A finely ground sample was extruded from a metal block in the form of a rod 0.5 mm. in diameter. Tables I, II and III report interplanar spacings and the relative diffraction intensities for the several isomeric pairs.

Analyses of Mixtures.—Mixtures were prepared by dissolving the pure components of a given isomeric pair in a suitable solvent (acetone was used for the 9,10-epoxysearic acids and 9,10-epoxyoctadecanols; absolute eth-

TABLE IV
MELTING RANGE-COMPOSITION OF MIXTURES OF ISOMERIC PAIRS

High melting isomer, %	Melting range, °C.
9,10-Epoxysearic acids	
100.0	58.0-58.7
93.28	55.8-57.6
74.84	46.5-54.5
51.63	46.3-50.4
51.58	45.9-50.0
41.66	45.8-49.2
20.48	47.4-51.9
5.97	49.0-54.5
0	54.1-55.0
9,10-Epoxyoctadecanols	
100.0	52.6-53.5
73.43	41.4-50.2
50.83	41.0-45.6
45.59	41.2-43.3
25.09	40.4-46.0
0	48.0-48.8
9,10-Dihydroxystearic acids	
100.0	130.7-131.0
90.68	124-128.4
75.58	115-125.8
48.25	92-117.5
31.61	92-110.9
25.17	92.5-94.7
15.20	92.1-93.1
7.32	92.9-93.7
0	94.7-95.1

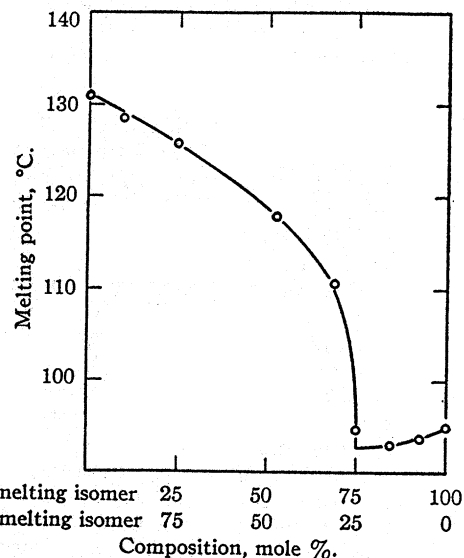


Fig. 3.—9,10-Dihydroxystearic acids, melting point-composition.

anol for the 9,10-dihydroxystearic acids). Crystalline mixtures were obtained by evaporation, first at atmospheric pressure and room temperature, and then under vacuum. The solidified mixture was then finely powdered. Melting points were determined by the capillary method. Within the melting range of the mixture, the temperature was raised at a rate not exceeding 0.25° per minute. Table IV gives the melting ranges of mixtures of the three isomeric pairs. Figures 1, 2, 3 are the melting point-composition diagrams. In making melting point-composition diagrams for use in the analyses of unknown mixtures, the melting points plotted were the temperatures at which the last crystals fused.

The composition of mixtures of the isomeric 9,10-dihydroxystearic acids was determined from the intensity of the 9.77 Å. diffraction line of the low melting isomer relative to that of the 10.43 Å. diffraction line of the high melting isomer. This quantity, designated I_{low}/I_{high} , is plotted as a function of composition in Fig. 4. The relative intensities were measured by a microdensitometer.

Duplicate measurements were made on each side of the powder photographs.

Results and Discussion

The interplanar spacings and relative intensities reported in Tables I, II and III show that each isomer can be readily distinguished and identified by the X-ray diffraction data. Table V gives the crystal long spacings calculated from these data.

TABLE V
LONG SPACINGS OF ISOMERIC PAIRS

Compound	Long spacing, Å.
<i>cis</i> -9,10-Epoxyoctadecanol, m. p. 52.6–53.5° (from oleyl alcohol)	44.99
<i>trans</i> -9,10-Epoxyoctadecanol, m. p. 48.0–48.8° (from elaidyl alcohol)	49.45
<i>cis</i> -9,10-Epoxyoctadecanoic acid, m. p. 58.1–58.7° (from oleic acid)	45.34
<i>trans</i> -9,10-Epoxyoctadecanoic acid, m. p. 54.1–55° (from elaidic acid)	47.09
9,10-Dihydroxyoctadecanoic acid, m. p. 131° (from oleic acid- <i>cis</i> hydroxylation)	41.77
9,10-Dihydroxyoctadecanoic acid, m. p. 95° (from elaidic acid- <i>cis</i> hydroxylation)	39.09

From X-ray diffraction studies of the *n*-aliphatic acids^{12,13} and the *n*-aliphatic alcohols,¹⁴ it has been observed that these molecules crystallize in bimolecular layers and that the long spacings measured on the diffraction photographs are the projection of double the molecular length on $[d_{001}]$. The measured long spacing and the dimer length are identical only when the dimer length is perpendicular to the 001 plane, that is, when the acid or alcohol crystallizes in the vertical form. If this is the case in a system under investigation, a comparison of the dimer lengths calculated from known bond distances and angles and from the measured long spacing should identify the *cis* and *trans* components of isomeric pairs.

Wilson and Ott¹⁵ observed that one crystalline modification of *n*-aliphatic alcohols crystallized from solvent with the *c* axis approximately perpendicular to the 001 plane. They used a projected C–C distance of 1.27 Å. and a projected C–O distance of 1.17 Å. and found that the projected distance between centers of carbons of terminal methyl groups was 2.54 Å. and the projected distance between neighboring OH groups was 1.46 Å. If these distances are taken from Wilson and Ott's work, the only other quantities necessary to calculate the maximum

length of a dimeric epoxyoctadecanol are the C–C distance in the oxirane ring and the angle that the chain segments make with the plane of the ring. A C–C distance of 1.4728 Å. has been reported recently¹⁶ for deuterated ethylene oxide, together with additional data, from which we have calculated that the angle made by the hydrogen with the plane of the oxirane ring is 119° 3'. Assuming these values to be the same in the epoxyoctadecanols as in ethylene oxide, we computed the maximum length of a dimer of *trans*-9,10-epoxyoctadecanol to be 49.6 Å. A similar calculation for the *cis* isomer gave 45.3 Å., when the normal zigzag structure was assumed. A more extended model, with calculated length 46.2 Å., is possible by a 180° rotation about carbon atom 12 or 7. The measured long spacing for 9,10-epoxyoctadecanol, m. p. 48.0–48.8°, is 49.45 Å., in excellent agreement with the value (49.6 Å.) calculated for the *trans* structure. Furthermore, there is apparently no configuration of *cis*-9,10-epoxyoctadecanol whose dimer approximates 49.45 Å. in length. This proves that the low-melting 9,10-epoxyoctadecanol, m. p. 48.0–48.8°, must possess the *trans* configuration and that the dimer axis is approximately perpendicular to the 001 plane. Since elaidyl alcohol has the *trans* configuration, it follows that epoxidation must pro-

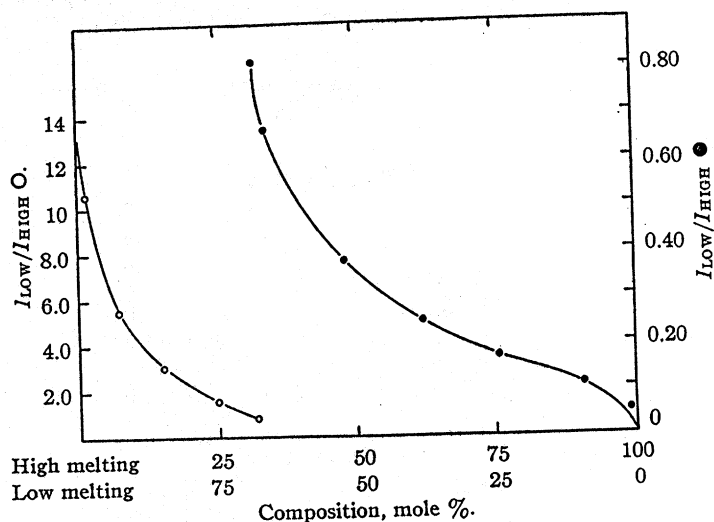


Fig. 4.—Intensity of 9.77 Å. line of low melting 9,10-dihydroxy-stearic acid relative to the intensity of the 10.43 Å. line of the high melting isomer as a function of composition.

ceed by *cis* addition, as was previously concluded.³ The measured long spacing of 44.99 Å. for *cis*-9,10-epoxyoctadecanol, m. p. 52.6–53.5°, is in good agreement with the value of 45.3 Å., calculated for the normal zigzag structure. The same experimental long spacing, however, would be obtained if the model assumed to have 180°.

(12) Müller, *J. Chem. Soc.*, **123**, 2043 (1923).

(13) Müller and Shearer, *ibid.*, **123**, 316 (1923).

(14) Malkin, *THIS JOURNAL*, **52**, 3739 (1930).

(15) Wilson and Ott, *J. Chem. Phys.*, **2**, 231, 239 (1934).

(16) Cunningham, Boyd, Gwinn and Le Van, *J. Chem. Phys.*, **17**, 211 (1949).

rotation about either carbon atom 12 or 7 was tilted with respect to the 001 plane.

The long spacings of the isomeric 9,10-epoxy- and 9,10-dihydroxystearic acids cannot be similarly used to reveal the configuration. The configuration of the isomeric 9,10-epoxystearic acids, however, has been inferred by analogy from the data on the isomeric epoxyoctadecanols because of the structural similarity of the pairs of parent compounds and the parallel course of the epoxidation reactions. The calculated length of the extended dimer of *trans*-9,10-epoxystearic acid, m. p. 54.1–55°, is 50.7 Å., and that of the *cis* isomer, m. p. 58.1–58.7°, is 46.3 Å., with the normal zigzag structure assumed. A length of 47.3 Å. was calculated for the *cis* isomer with maximum extension (180° rotation about either carbon atom 12 or 7). Since the measured long spacing for the *cis* isomer is 45.3 Å. and that for the *trans* isomer is 47.1 Å., it is evident that the dimers are considerably tilted with respect to the 001 plane, as is common among long chain aliphatic acids.^{12,13}

The assignment of the *trans* configuration to the low melting 9,10-epoxystearic acid is substantiated by the infrared spectra.¹⁷ *trans*-9,10-Epoxyoctadecanol, from elaidyl alcohol has an absorption peak at 11.4 microns, and the low-melting 9,10-epoxystearic acid from elaidic acid also has an absorption peak at this wave length. The corresponding peaks for the high melting *cis* compounds, 9,10-epoxyoctadecanol from oleyl alcohol and 9,10-epoxystearic acid from oleic acid, appear at 11.8 microns. The configurations assigned to the isomeric pairs of oxirane compounds are listed in Table V.

The long spacings of the isomeric 9,10-dihydroxystearic acids are appreciably different, 41.77 Å. for the isomer with m. p. 131°, and 39.09 Å. for the isomer with m. p. 95°. Both spacings are so much smaller than the computed maximum length of the dimeric acids, 50.6 Å., it is clear that the acids crystallize with low angles of tilt.

Table IV and Figs. 1, 2 and 3 give melting point-composition data for the three isomeric pairs investigated. The composition of a binary mixture of either the isomeric 9,10-epoxyoctadecanols or the isomeric 9,10-epoxystearic acids can be determined in the usual way to about $\pm 1\%$ from the melting point-composition curves. For analyzing mixtures of the isomeric 9,10-dihydroxystearic acids, however, melting point-composition data are of little value because over a wide range of composition the melting range was 10–20° and some difficulty was experienced in duplicating the temperature of disappearance of the last crystal.

(17) Shreve, Hechter, Knight and Swern, American Chemical Society, 116th National Meeting, Atlantic City, N. J., September 18–23, 1949.

X-Ray diffraction was then tried as a means of analysis. The isomeric 9,10-dihydroxystearic acids have different crystal structures, as evidenced by their diffraction patterns (Table I), and the experimental data in Fig. 4 indicate no mutual solubility of the isomers when crystallized from solution. Powder patterns of mixtures containing as little as 1% of either isomer showed the characteristic diffraction spectra of each isomer, and the interplanar spacings measured were the same as those of the pure isomers, within the limits of experiment error. Table I gives spacings for the pure isomers and a mixture containing 75% low-melting 9,10-dihydroxystearic acid and 25% high melting dihydroxystearic acid. A comparison of the intensities of the 9.77 Å. and 10.43 Å. diffraction lines permits the composition to be determined to within $\pm 3\%$.

Acknowledgment.—The authors are indebted to R. E. Koos for the preparation of the isomers.

Summary

X-Ray diffraction and melting point-composition data are reported for the isomeric 9,10-epoxy- and dihydroxystearic acids and the isomeric 9,10-epoxyoctadecanols. Each member of an isomeric pair can be readily and positively identified by the position and intensity of the X-ray diffraction lines.

The geometric configuration of the 9,10-epoxyoctadecanols has been established by a comparison of calculated and observed long spacings. The low melting isomer, m. p. 48.0–48.8°, possesses the *trans* configuration, and the high melting isomer, m. p. 52.6–53.5°, the *cis* configuration.

Long spacings of the isomeric 9,10-epoxystearic acids could not be employed in assigning a definite configuration because the molecules are tilted with respect to the diffracting planes. By analogy with the 9,10-epoxyoctadecanols, however, the geometric configuration of low-melting 9,10-epoxystearic acid, m. p. 54.1–55°, is *trans*, and that of the high melting isomer, m. p. 58.1–58.7°, is *cis*. Infrared spectra substantiate this assignment.

Melting point-composition data can be employed in determining the composition of binary mixtures of the isomeric 9,10-epoxyoctadecanols and 9,10-epoxystearic acids to $\pm 1\%$. Similar data for the isomeric 9,10-dihydroxystearic acids are of little value for analytical purposes. The powder patterns of such mixtures, however, show the characteristic lines of each isomer even when as little as 1% is present, and the composition can be determined to $\pm 3\%$ from the relative intensity of a selected pair of diffraction lines.